

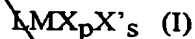
## CLAIMS

1. A multi-stage process for the polymerization of olefins comprising:
- (I) a first polymerization stage, wherein one or more olefins of formula  $\text{CH}_2=\text{CHR}$ , wherein R is hydrogen or a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{10}$  alkyl, cycloalkyl or aryl radical, are polymerized in one or more reactors, in the presence of a catalyst comprising the product of the reaction between an alkyl-Al compound and a solid component comprising at least one compound of a transition metal  $\text{M}^{\text{I}}$  chosen between Ti and V, and not containing  $\text{M}^{\text{I}}-\pi$  bonds, and a halide of Mg, in order to produce an olefinic polymer having porosity, expressed as percentage of voids, greater than 5%;
- (II) a treatment stage, wherein the product obtained in said first polymerization stage (I) is, in any order whatever:
- (a) optionally contacted with a compound capable of deactivating the catalyst used in stage (I); and
- (b) contacted with a late transition metal complex, optionally in the presence of a suitable activating agent; and
- (III) a second polymerization stage, wherein one or more olefinic monomers are polymerized in one or more reactors, in the presence of the product obtained from stage (II).
2. The multi-stage process according to claim 1 wherein, in stage (I), said alkyl-Al compound is a trialkyl-Al, an alkyl-Al halide or an alkyl-Al sesquichloride, said halide of Mg is  $\text{MgCl}_2$  and said compound of a transition metal  $\text{M}^{\text{I}}$  is selected from the group consisting of halides of Ti, halo alkoxides of Ti,  $\text{VCl}_3$ ,  $\text{VCl}_4$ ,  $\text{VOCl}_3$  and halo alkoxides of V.
3. The multi-stage process according to claim 2, wherein said compound of a transition metal  $\text{M}^{\text{I}}$  is selected from the group consisting of  $\text{TiCl}_4$ ,  $\text{TiCl}_3$  and halo alkoxides of the formula  $\text{Ti}(\text{OR}^{\text{I}})_m\text{X}_n$ , wherein  $\text{R}^{\text{I}}$  is a  $\text{C}_1\text{-C}_{12}$  hydrocarbon radical or a  $-\text{COR}^{\text{I}}$  group, X is halogen and  $(m+n)$  corresponds to the oxidation state of Ti.
4. The multi-stage process according to claim 1 wherein, in stage (I), said solid component is in the form of spherical particles having a mean diameter ranging from 10  $\mu\text{m}$  to 150  $\mu\text{m}$ .
5. The multi-stage process according to claim 1, wherein the catalyst used in stage (I) comprises the product of the reaction between an Al-alkyl compound, an electron-donating compound (external donor) and a solid component comprising at least one compound of a transition metal  $\text{M}^{\text{I}}$  selected from Ti and V and not containing  $\text{M}^{\text{I}}-\pi$  bonds, a magnesium halide and an

**electron-donating compound (internal donor).**

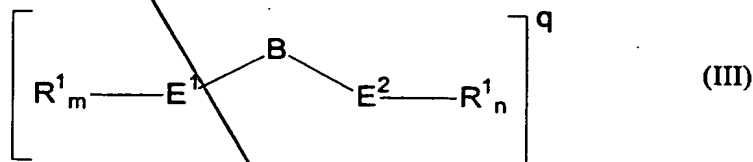
6. The multi-stage process according to claim 1, wherein the porosity of the olefinic polymer obtained in the first polymerization stage (I) is greater than 10%.
7. The multi-stage process according to claim 6, wherein more than 40% of said porosity is due to pores with diameter greater than 10,000 Å.
8. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(a), said compound capable of deactivating the catalyst used in stage (I) has formula  $R^{IV}_yXH$ , wherein  $R^{IV}$  is hydrogen or a  $C_1$ - $C_{10}$  hydrocarbon radical, X is O, N, or S, and y corresponds to the valence of X.
9. The multi-stage process according to claim 8, wherein said compound capable of deactivating the catalyst used in stage (I) is selected from the group consisting of  $H_2O$ ,  $NH_3$ ,  $H_2S$ ,  $CO$ ,  $COS$ ,  $CS_2$ ,  $CO_2$  and  $O_2$ .

10. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(b), said late transition metal complex has formula (I) or (II):



wherein M is a metal belonging to Group 8, 9, 10 or 11 of the Periodic Table;

**L is a bidentate or tridentate ligand of formula (III):**



wherein:

B is a C<sub>1</sub>-C<sub>50</sub> bridging group linking E<sup>1</sup> and E<sup>2</sup>, optionally containing one or more atoms belonging to Groups 13-17 of the Periodic Table;

E<sup>1</sup> and E<sup>2</sup>, the same or different from each other, are elements belonging to Group 15 or 16 of the Periodic Table and are bonded to said metal M;

the substituents R<sup>1</sup>, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> alkyliden, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl and C<sub>7</sub>-C<sub>20</sub> arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table of the Elements (such as B, Al, Si, Ge, N, P, O, S, F and Cl atoms); or two R<sup>1</sup> substituents attached to the same atom E<sup>1</sup> or E<sup>2</sup> form a saturated, unsaturated or aromatic C<sub>4</sub>-C<sub>8</sub> ring, having from 4 to 20 carbon atoms;

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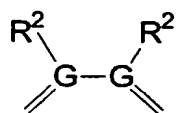
$m$  and  $n$  are independently 0, 1 or 2, depending on the valence of  $E^1$  and  $E^2$ , so to satisfy the valence number of  $E^1$  and  $E^2$ ;  $q$  is the charge of the bidentate or tridentate ligand so that the oxidation state of  $MX_pX'_s$  or MA is satisfied, and the compound (I) or (II) is overall neutral;  $X$ , the same or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen,  $-R$ ,  $-OR$ ,  $-OSO_2CF_3$ ,  $-OCOR$ ,  $-SR$ ,  $-NR_2$  and  $-PR_2$  groups, wherein the  $R$  substituents are linear or branched, saturated or unsaturated,  $C_1$ - $C_{20}$  alkyl,  $C_3$ - $C_{20}$  cycloalkyl,  $C_6$ - $C_{20}$  aryl,  $C_7$ - $C_{20}$  alkylaryl or  $C_7$ - $C_{20}$  arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table of the Elements (new IUPAC notation), such as B, N, P, Al, Si, Ge, O, S and F atoms; or two  $X$  groups form a metallacycle ring containing from 3 to 20 carbon atoms; the substituents  $X$  are preferably the same;

$X'$  is a coordinating ligand selected from mono-olefins and neutral Lewis bases wherein the coordinating atom is N, P, O or S;

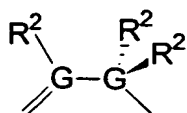
$p$  is an integer ranging from 0 to 3, so that the final compound (I) or (II) is overall neutral;

$s$  ranges from 0 to 3; and  $A$  is a  $\pi$ -allyl or a  $\pi$ -benzyl group.

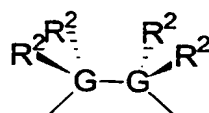
11. The multi-stage process according to claim 10, wherein said bridging group B is selected from the group consisting of:



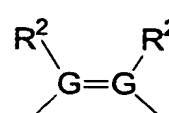
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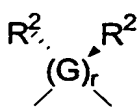
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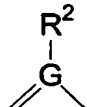
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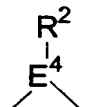
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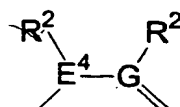
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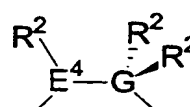
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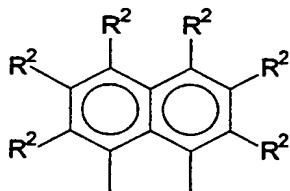
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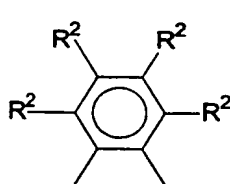
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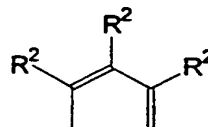
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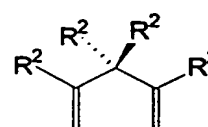
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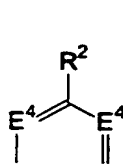
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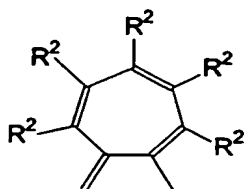
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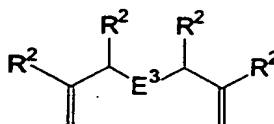
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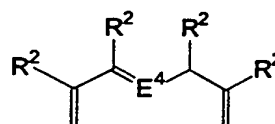
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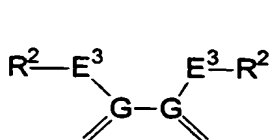
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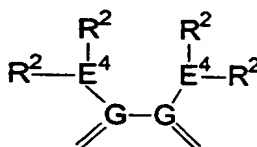
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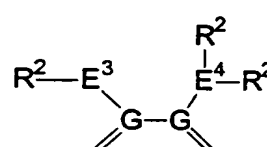
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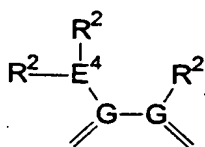
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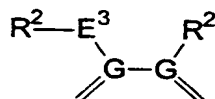
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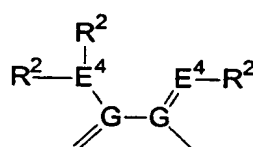
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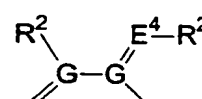
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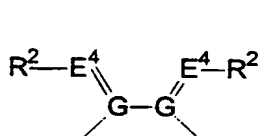
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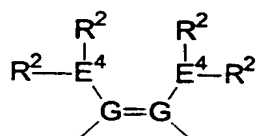
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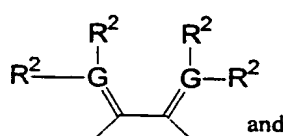
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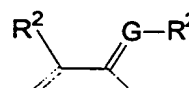


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and



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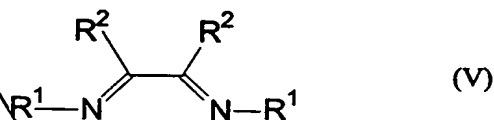
wherein G is an element belonging to Group 14 of the Periodic Table; r is an integer ranging from 1 to 5; E<sup>3</sup> is an element belonging to Group 16 and E<sup>4</sup> is an element belonging to Group 13 or 15 of the Periodic Table; the substituents R<sup>2</sup>, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl and C<sub>7</sub>-C<sub>20</sub> arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; or two R<sup>2</sup> substituents form a saturated, unsaturated or aromatic C<sub>4</sub>-C<sub>8</sub> ring, having from 4 to 20 carbon atoms, or they form a polycyclic ring system, optionally containing one or more Group 13-16 elements; a substituent R<sup>1</sup> and a substituent R<sup>2</sup> may form a substituted or unsubstituted, saturated, unsaturated or aromatic

**C<sub>4</sub>-C<sub>8</sub> ring, having from 4 to 20 carbon atoms and optionally containing one or more Group 13-16 element.**

12. The multi-stage process according to claim 10, wherein E<sup>1</sup> and E<sup>2</sup> are selected from the group consisting of N, P, O, and S.

13. The multi-stage process according to claim 10, wherein the substituents R<sup>1</sup> are C<sub>6</sub>-C<sub>20</sub> aryl groups; the substituents X are selected from the group consisting of hydrogen, methyl, phenyl, Cl, Br and I; and p is 1, 2 or 3.

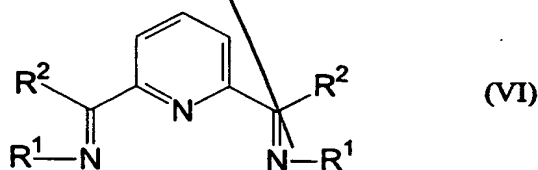
14. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (V):



wherein R<sup>1</sup> and R<sup>2</sup> have the meaning reported in claims 10 and 11; M belongs to Group 10 of the Periodic Table; X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

15. The multi-stage process according to claim 14, wherein the substituents R<sup>1</sup> are C<sub>6</sub>-C<sub>20</sub> aryl groups, optionally substituted in the 2 and 6 positions with alkyl groups containing 1 to 20 carbon atoms and/or halo groups; the substituents R<sup>2</sup> are selected from the group consisting of hydrogen, methyl, ethyl, n-propyl, i-propyl and benzyl, or the two substituents R<sup>2</sup> form together an acenaphtenquinone group.

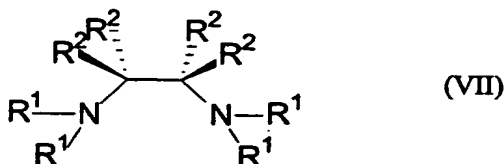
16. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (VI):



wherein the R<sup>1</sup> and R<sup>2</sup> groups have the meaning reported in claims 10 and 11, the metal M is Fe or Co; the X radicals are preferably hydrogen, methyl, Cl Br or I; p is 2 or 3; and s is 0.

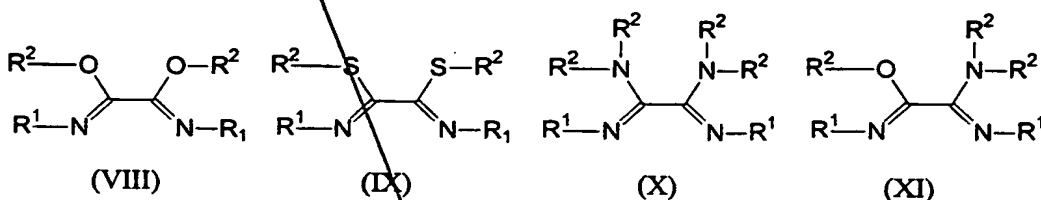
17. The multi-stage process according to claim 16, wherein the substituents  $R^2$  are hydrogen or methyl, and the substituents  $R^1$  are aryl rings.

18. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (VII):



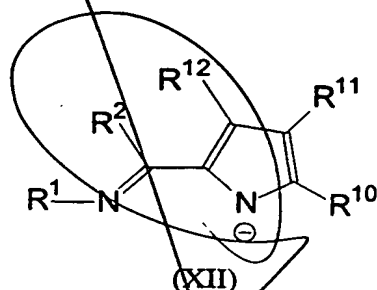
wherein  $R^1$  and  $R^2$  have the meaning reported in claims 10 and 11, M belongs to group 10 of the Periodic Table, the X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

19. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to one of formulae (VIII)-(XI):



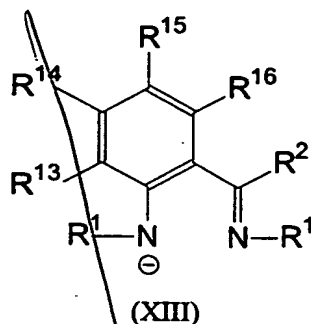
wherein  $R^1$  and  $R^2$  have the meaning reported in claims 10 and 11, M belongs to Group 10 of the Periodic Table, the X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

20. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XII):



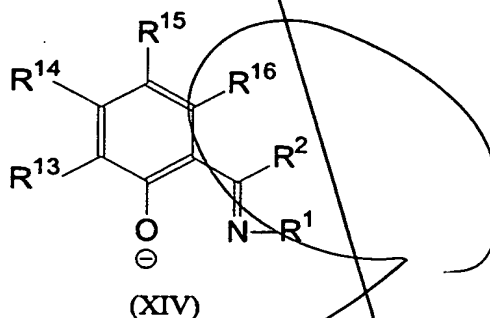
wherein  $R^1$  and  $R^2$  have the meaning reported in claims 10 and 11;  $R^{10}$ - $R^{12}$ , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$  alkyl,  $C_3$ - $C_{20}$  cycloalkyl,  $C_6$ - $C_{20}$  aryl,  $C_7$ - $C_{20}$  alkylaryl and  $C_7$ - $C_{20}$  arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; or two adjacent substituents  $R^{10}$ - $R^{12}$  form a saturated, unsaturated or aromatic  $C_4$ - $C_8$  ring, having from 4 to 40 carbon atoms; the metal M is preferably Fe, Co, Rh, Ni or Pd; the X radicals are hydrogen, methyl, Cl Br or I; p is 2 or 3; and s is 0.

21. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XIII):



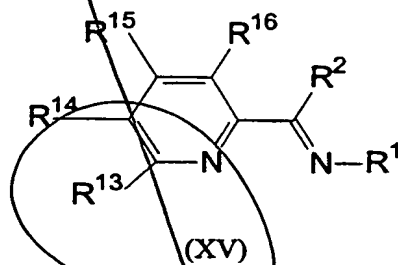
wherein  $R^1$  and  $R^2$  have the meaning reported in claims 10 and 11; the substituents  $R^{14}$  and  $R^{16}$ , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$  alkyl,  $C_3$ - $C_{20}$  cycloalkyl,  $C_6$ - $C_{20}$  aryl,  $C_7$ - $C_{20}$  alkylaryl and  $C_7$ - $C_{20}$  arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; the substituents  $R^{13}$  and  $R^{15}$ , the same or different from each other, have the same meaning of substituents  $R^{14}$  and  $R^{16}$ , optionally forming with an adjacent substituent  $R^{14}$  or  $R^{16}$  a saturated, unsaturated or aromatic  $C_4$ - $C_8$  ring, or they are electron withdrawing groups; the metal  $M$  is Fe, Co, Ni or Pd; the  $X$  radicals are hydrogen, methyl, Cl Br or I;  $p$  is 2 or 3; and  $s$  is 0.

22. The multi-stage process according to claims 10 and 11, wherein said ligand  $L$  corresponds to formula (XIV):



wherein  $R^1$  and  $R^2$  have the meaning reported in claims 10 and 11;  $R^{14}$  and  $R^{16}$ , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$  alkyl,  $C_3$ - $C_{20}$  cycloalkyl,  $C_6$ - $C_{20}$  aryl,  $C_7$ - $C_{20}$  alkylaryl and  $C_7$ - $C_{20}$  arylalkyl radical, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table;  $R^{13}$  and  $R^{15}$ , the same or different from each other, have the same meaning of  $R^{14}$  and  $R^{16}$ , optionally forming with an adjacent  $R^{14}$  or  $R^{16}$  a saturated, unsaturated or aromatic  $C_4$ - $C_8$  ring, or they are electron withdrawing groups; the metal  $M$  belongs to Group 10 of the Periodic Table, the  $X$  radicals are hydrogen, methyl,

- allyl, Cl, Br or I, A is a C<sub>3</sub>-C<sub>5</sub> linear allyl, p is 1 and s is 1.
23. The multi-stage process according to claim 22 wherein, in said ligand of formula (XIV), R<sup>1</sup> is aryl, substituted in the 2, 6 and/or 4 positions with a substituent selected from halogen and linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, or is a tertiary C<sub>3</sub>-C<sub>6</sub> alkyl group; R<sup>2</sup> is hydrogen or methyl; R<sup>14</sup> and R<sup>16</sup> are hydrogen, methyl or methoxy; R<sup>13</sup> is selected from the group consisting of aryl, substituted in the 2 and 6 positions with branched C<sub>3</sub>-C<sub>30</sub> alkyl groups, tertiary C<sub>3</sub>-C<sub>6</sub> alkyl group, -NO<sub>2</sub> and halo; and R<sup>15</sup> is selected from the group consisting of aryl, tertiary C<sub>3</sub>-C<sub>6</sub> alkyl group, -NO<sub>2</sub>, halo, -CF<sub>3</sub>, -SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub>R and -COO<sup>-</sup>.
24. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XV):



- wherein R<sup>1</sup> and R<sup>2</sup> have the meaning reported in claims 10 and 11; the substituents R<sup>14</sup> and R<sup>16</sup>, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl and C<sub>7</sub>-C<sub>20</sub> arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; the substituents R<sup>13</sup> and R<sup>15</sup>, the same or different from each other, have the same meaning of substituents R<sup>14</sup> and R<sup>16</sup>, optionally forming with an adjacent substituent R<sup>14</sup> or R<sup>16</sup> a saturated, unsaturated or aromatic C<sub>4</sub>-C<sub>8</sub> ring, or they are electron withdrawing groups; the metal M belongs to Group 10 of the Periodic Table; the X radicals are hydrogen, methyl, Cl, Br or I, p is 2 or 3, s is 0.
25. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(b), said activating agent is an alumoxane and/or a compound able to form an alkylmetal cation.
26. The multi stage process according to claim 1 wherein, in the treatment stage (II), the product obtained in the first polymerization stage (I) is, in the following order:
- first contacted with said compound capable of deactivating the catalyst used in stage (I); and
  - then contacted with said late transition metal complex, optionally in the presence of a suitable activating agent.
27. The multi-stage process according to claim 26 wherein, before step (b), any excess of said



- compound capable of deactivating the catalyst used in stage (I) is removed.
28. The multi-stage process according to claim 1, wherein the polymerization stage (I) is carried out in liquid phase, said liquid phase consisting of a hydrocarbon solvent or of one or more olefins  $\text{CH}_2=\text{CHR}$ , and the polymerization stage (III) is carried out in gas phase, in at least one reactor with a fluidized bed or a mechanically-agitated bed.
29. The multi-stage process according to claim 1, wherein both polymerization stages (I) and (III) are carried out in gas phase, in reactors with a fluidized bed or a mechanically-agitated bed.
30. A catalyst component for the polymerization of olefins comprising a late transition metal complex supported on a polymeric porous support having a porosity, expressed as percentage of voids, greater than 5%.
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31. A catalyst component for the polymerization of olefins comprising a late transition metal complex supported on a polymeric porous support having a porosity, expressed as percentage of voids, greater than 5%, said catalyst component being obtainable by a process comprising:
- (I) a polymerization stage, wherein one or more olefins of formula  $\text{CH}_2=\text{CHR}$ , wherein R is hydrogen or a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{10}$  alkyl, cycloalkyl or aryl radical, in the presence of a catalyst comprising the product of the reaction between one or more alkyl-Al compounds and a solid component comprising at least one compound of a transition metal  $\text{M}^{\text{I}}$  chosen between Ti and V, and not containing  $\text{M}^{\text{I}}\text{-}\pi$  bonds, and a halide of Mg;
  - (II) a treatment stage, wherein the product obtained in the polymerization stage (I) is, in any order whatever:
    - (a) optionally contacted with one or more compounds capable of deactivating the catalyst used in step (I); and
    - (b) contacted with one or more late transition metal complexes, optionally in the presence of a suitable activating agent.
32. The catalyst component according to claim 30 or 31, wherein said late transition metal complex is supported in a quantity ranging from  $1.10^{-7}$  to  $1.10^{-1}$  mmol per gram of polymeric porous support.
33. The catalyst component according to claim 30 or 31, wherein said polymeric porous support has a porosity greater than 10%.
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34. The catalyst component according to claim 33, wherein more than 40% of the porosity is due to pores with diameter greater than  $10,000 \text{ \AA}$ .
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35. A polymer composition obtainable with the process of claim 1, characterized in that:

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Cont.
- in said first polymerization stage a homo or copolymer of propylene is obtained, having a content of propylene units greater than 80% wt. and cold xylene soluble fractions lesser than 40% wt., said homo or copolymer of propylene consisting of 10-90 %wt. of the total amount of polymer; and
  - in said second polymerization stage amorphous polyethylene is produced, having a number of total branching greater than 50 branches/1000 C, a density ranging from 0.830 and 0.880 g/cm<sup>2</sup>, and a Tg value lesser than -30°C.

36. A polymer composition obtainable with the process of claim 1, characterized in that:

- in said first polymerization stage polyethylene, polypropylene or propylene/ethylene copolymer is produced, consisting of 10-90 %wt. of the total amount of polymer; and
- in said second polymerization stage block polyethylene is produced, having a melting point ranging from 100 to 130°C and a Tg value lesser than -30°C.

37. A polymer composition obtainable with the process of claim 1, characterized in that:

- in said first polymerization stage, a copolymer of ethylene with one or more  $\alpha$ -olefins (LLDPE) is obtained, having a content of ethylene units of 80-99%wt., said copolymer of ethylene consisting of 10-90 %wt. of the total amount of polymer;
- in the second polymerization stage, polyethylene is produced having a number of total branching greater than 5 branches/1000 C and a density greater than 0.880 g/cm<sup>3</sup>.

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